

CLAIMS

What is claimed is:

1. Crosslinked microparticles of between 10 and 300 nm in size, obtained by polymerization of a composition of ethylenically unsaturated polymerizable compounds, the composition of polymerizable compounds comprising:
 - a first component A representing from 50 to 99 mol% of the composition and selected from the group consisting of isobornyl (meth)acrylate, norbornyl (meth)acrylate, cyclohexyl (meth)acrylate, Cardura E10 (meth)acrylate and combinations thereof, optionally in combination with a C₂-C₈ alkyl (meth)acrylate
 - a second component B consisting of at least one monomer or oligomer comprising at least two ethylenic unsaturations which can undergo radical-mediated polymerization, the monomer or oligomer being other than an allylic(meth)acrylate
 - a third component C consisting of at least one monomer or oligomer comprising, in addition to an ethylenic unsaturation which can undergo radical-mediated polymerization, at least one reactive function f₁ which is different from the ethylenic unsaturation optionally with at least partial chemical modification of the initial functions f₁ into final functions f₂ under the condition that the functions f₁ selected do not react with each other during the polymerization, with the sum of the components A, B and C being 100 mol%.
2. The microparticles of Claim 1, wherein functions f₁ borne by the component C are selected from the group consisting of: epoxy, hydroxyl, carboxyl, carboxylic anhydride, isocyanate, silane, amine, oxazoline, and, where appropriate, functions f₁ at least partially modified into functions f₂, selected from: (meth)acrylates, vinyls, maleates, maleimides, itaconates, allylic alcohol esters,

unsaturations based on dicyclopentadiene, C₁₂-C₂₂ unsaturated fatty esters or amides, carboxylic acid salts and quaternary ammonium salts.

3. The microparticles of Claim 1 wherein component C is present in a molar content of between 0 and 49.5 mol% relative to the sum of the polymerizable compounds, and is selected from the group consisting of: glycidyl (meth)acrylate, C₂-C₆ hydroxyalkyl (meth)acrylates, (meth)acrylic acid, maleic acid or anhydride or fumaric acid, itaconic acid or anhydride, isocyanatoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, and 2-(5-methacryloyl-pentyl)-1,3-oxazoline.

4. The microparticles of Claim 1 wherein component B is selected from multifunctional (meth)acrylate monomers of functionality ranging from 2 to 6, substituted or unsubstituted divinylbenzenes and/or multifunctional (meth)acrylic ester oligomers or unsaturated polyesters of functionality ranging from 2 to 50 and with a number average molecular weight Mn of less than 2500.

5. The microparticles of Claim 1 wherein the composition of the polymerizable compounds comprises:

- 50 to 95 mol% of a component A selected from the group consisting of isobornyl (meth)acrylate, norbornyl (meth)acrylate, butyl (meth)acrylate and combinations thereof
- 0.5 to 10 mol% of a component B consisting of at least one monomer and/or oligomer selected from:
 - di(meth)acrylates of: ethylene glycol, propylene glycol, butanediol, 2-methylpropanediol, neopentyl glycol, hexanediol, diol oligomers with an Mn of less than 2500, preferably polyethers, polyesters or polyurethanes
 - substituted or unsubstituted divinylbenzenes
 - unsaturated polyester oligomers or acrylated acrylic oligomers with an Mn of less than 2500

and having a number of ethylenic unsaturations per mole of from 2 to 50

- not more than 49.5 mol% of a component C consisting of at least one monomer and/or oligomer selected from:

- (meth)acrylic acid, maleic, fumaric or itaconic acid, when f1 is a carboxyl function;
- maleic anhydride or itaconic anhydride when, f1 is a carboxylic anhydride function;
- hydroxyalkyl (meth)acrylates containing a C₂-C₆ alkyl or mono (meth) acrylates of polyether or polyester or polyurethanediol or polycaprolactone oligomers with an Mn of less than 1500, when f1 is a hydroxyl function;
- glycidyl (meth)acrylate, (meth)acrylates of epoxidized derivatives of dicyclopentadiene or epoxidized vinylbornene (meth)acrylates or alkoxyglycidyl ether (meth)acrylates or (meth)acrylates of epoxidized derivatives of cyclohexene, when f1 is an epoxy function;
- isocyanatoethyl (meth)acrylate and urethane mono (meth) acrylates derived from diisocyanates, when f1 is an isocyanate function;
- (meth)acrylates bearing a trialkyl or trialkoxysilane group, when f1 is a silane function;
- dimethylaminoethyl (meth)acrylate or tert-butylaminoethyl (meth)acrylate, when f1 is an amine function;
- 2-(5-(meth)acryloylpentyl)-1, 3-oxazoline, when f1 is a oxazoline function;

with the sum A + B + C being equal to 100 mol%.

6. The microparticles according to Claim 1 wherein f1 is carboxyl functions or hydroxyl functions which are partially or totally modified into functions f2 selected from the group consisting of: (meth)acrylate, vinyl, maleate, fumarate, maleimide, carboxylic acid salt or combinations thereof.

7. The microparticles of Claim 1 wherein they bear hydroxyl or epoxy functions f1 possibly partially modified into (meth)acrylate functions f2.

8. A process for preparing the microparticles as defined in Claim 1, the process comprising the steps of:

- polymerizing, via radical-mediated dispersion polymerization, in a non-aqueous medium which is a nonsolvent for the polymer formed, a composition of polymerizable compounds as defined in Claim 1, without any addition of a stabilizing polymer for the microparticles formed, either before, during or after polymerization and optionally,

- chemically modifying, at least partially, the functions f1 borne by the component C.

9. A coating, moulding or composite composition, comprising the microparticles of Claim 1.

10. The composition of Claim 9 consisting essentially of the microparticles of Claim 1 comprising functions f1 and/or f2 which are identical or different and which can be crosslinked between microparticles, forming at least one crosslinking network.

11. The composition of Claim 9 comprising from 0.5 to 50% by weight of the microparticles of Claim 1.

12. The composition of Claim 9 wherein the composition is a coating composition.

13. The composition according to Claim 12 wherein the coating composition is a composition which can undergo radical-mediated crosslinking, comprising: (i) acrylic or vinyl mono-or

multifunctional monomers and/or multifunctional acrylic oligomers and (ii) the microparticles of Claim 1 bearing f2 functions selected from the group consisting of (meth)acrylate, maleate, fumarate, maleimide functions and combinations thereof, the f2 functions obtained from the at least partial modification of the starting functions f1.

14. The composition of Claim 12 wherein the coating composition is a composition which can undergo crosslinking by radiation.

15. The composition of Claim 13 wherein the crosslinkable composition comprises: (i) acrylic monomers selected from the group consisting of: isobornyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, 2-(2-ethoxyethoxy) ethyl (meth)acrylate, tridecyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate and combinations thereof, and/or (ii) at least one acrylic oligomer chosen from the group consisting of: polyether (meth)acrylates, polyester (meth)acrylates, polyurethane (meth)acrylates, polycaprolactone (meth)acrylates, epoxy (meth)acrylates and (meth) acrylated acrylic copolymers.

16. The coating composition of Claim 12, characterized in that it is intended to be applied or is applied in the form of a coating on polar or non-polar substrates and comprises:

- 0.5 to 50% and preferably from 5 to 30% by weight of the microparticles of Claim 1, having f2 functions selected from the group consisting of: (meth)acrylate, maleate, fumarate, maleimide and combinations thereof,
 - 50 to 99.5% by weight of at least one monomer chosen from: isobornyl (meth)acrylate, isodecyl (meth)acrylate; lauryl (meth)acrylate; or tridecyl (meth)acrylate,
 - 0 to 5% by weight of a C₂-C₆ alkylene diol di(meth)acrylate
- the percentages being chosen such that the total sum of the microparticles and monomers is equal to 100% by weight.

17. The coating composition according to Claim 16 wherein:

- the polar substrates are selected from the group consisting of: glass, steel, aluminum, silicon, polycarbonate, wood, glass fibres, carbon fibres, cellulose fibres, polyester or polyamide fibres;

- the non-polar substrates are selected from the group consisting of: polyolefins and more particularly polyethylene, polypropylene and ethylene/propylene copolymers with or without special surface treatment, and coatings of low surface tension.

18. The coating composition of Claim 16 applied to the substrate in the form of a thin film with a thickness of less than 100 microns.

19. The composition of Claim 12, wherein the coating composition is a composition of an aqueous dispersion of a crosslinkable polymer, comprising reactive water-dispersible or water-soluble microparticles, which participate in the crosslinking.

20. The coating composition of Claim 9, wherein the composition is a composition comprising epoxidized derivatives.

21. The coating composition of Claim 20, wherein the composition is crosslinkable by UV radiation in the presence of a cationic photo-initiator and comprises microparticles bearing epoxy and/or hydroxyl functions fl.

22. The coating composition of Claim 20, wherein the composition is crosslinkable by condensation reaction with at least one second reactive component selected from the group consisting of: polyamines, carboxy functionalized or carboxylic anhydride-functionalized polymers or copolymers; and combinations thereof.

23. The coating composition of Claim 20, when the composition can be

crosslinked by condensation reaction, the composition comprising microparticles having functions f1 and/or f2 selected from the group consisting of: epoxy; hydroxyl; carboxyl; anhydride; and combinations thereof.

24. The coating composition of Claim 9, wherein the composition comprises:

(i) at least one reactive resin selected from the group consisting of: alkyds, unsaturated polyesters, saturated polyesters, polyamides, polyurethanes and polyureas and (ii) the microparticles of Claim 1.

25. The moulding composition of Claim 9 further comprising: (i) at least one reactive resin selected from the group consisting of: unsaturated polyesters, dicyclopentadiene resins, vinyl esters, epoxides, polyamines, polyurethanes, polyureas and polyurethane-ureas; and (ii) the microparticles of Claim 1.

26. The moulding composition according to Claim 25, further comprising inorganic and/or organic fillers and/or reinforcing agents chosen from the group consisting of: glass fibres, glass mats, carbon fibres, cellulose fibres, polyester and polyamide fibres.

27. The coating composition of Claim 24 wherein the microparticles further comprise functions f1 and/or f2 that are reactive with at least one function borne by this or these reactive resin (s).

28. The moulding composition of Claim 25 wherein the microparticles further comprise functions f1 and/or f2 that are reactive with at least one function borne by this or these reactive resin (s).